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# PRODUCTS OF THE REACTION OF CHLORINE ATOMS AND OZONE

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16. ABSTRACT

Preliminary matrix-isolation infrared spectroscopic studies of the gas-phase reaction of chlorine atoms and ozone are reported. The major product of the reaction is found to be the symmetric OClO radical, while very little of the asymmetric ClOO radical is produced. It is also found that the presence of $O_2$ enhances the OClO production and that ClOO is the primary product in the reaction of Cl atoms and pure $O_2$. The radical ClO is also observed for the first time in a gas-phase reaction of Cl and $O_3$. A mechanism for these observations is proposed.

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## I. INTRODUCTION

Recently there has been much interest in the effect of catalytic cycles in stratospheric ozone chemistry [1-4]. The chlorine oxide ($Cl_xO_y$) cycle has been investigated to some extent, usually by postulating reaction mechanisms based upon reactions that these oxides are known to undergo and kinetics rate data (e.g., see Reference 4). However, while various mechanisms have been proposed, there is no firm experimental evidence that any of the proposed reaction intermediates are actually formed in the gas phase reaction of chlorine atoms and ozone. In our matrix isolation experiments, we are able to "trap" transient species on an argon matrix at 10°K and identify these species from their infrared spectra.

## II. PROCEDURE

Our procedure was to pre-make ozone by discharging pure $O_2$ (Linde 99.99 percent) at low pressure with a Tesla coil. The $O_3$ was then trapped in liquid nitrogen. The ozone was then pumped on for 0.5 hr to remove any oxygen. Our experiments included the reaction of Cl atoms with pure $O_3$, the reaction of Cl atoms with pure $O_2$, and the reaction of Cl atoms with $O_3/O_2$ mixtures of ratios 1:10, 1:20, and 1:60. Chlorine atoms were produced by microwave discharge of a 50:1 mixture of Ar and $Cl_2$ (Linde 99.99 percent). The Cl atoms and the $O_3/O_2$ mixtures were allowed to react (in the gas phase) in a kinetic cell of our design before deposition on a CsI cold window.

## III. RESULTS

The results of our experiments are as follows. In Figure 1 we give the infrared spectrum of the reaction of Cl atoms and pure $O_3$. The absorption at 1100 $cm^{-1}$ is due to symmetrical OClO [5]. There is no evidence for the production of ClOO; however, the absorption at 850 $cm^{-1}$ is assigned to the ClO radical [6]. The absorptions at 1300 $cm^{-1}$, 1245 $cm^{-1}$, and 800 $cm^{-1}$ to 740 $cm^{-1}$ are tentatively assigned to higher chlorine oxides ($ClO_x$) and are presently under investigation. In Figure 2 we give the infrared spectrum of chlorine atoms and pure $O_2$. There is an absorption at 1100 $cm^{-1}$ due to OClO, and the strong absorption at 1441 $cm^{-1}$ indicates the presence of ClOO [5].

Several experiments were performed at different $O_3/O_2$ concentrations (1:10, 1:20, 1:60, Figs. 3, 4, and 5, respectively). All experiments,

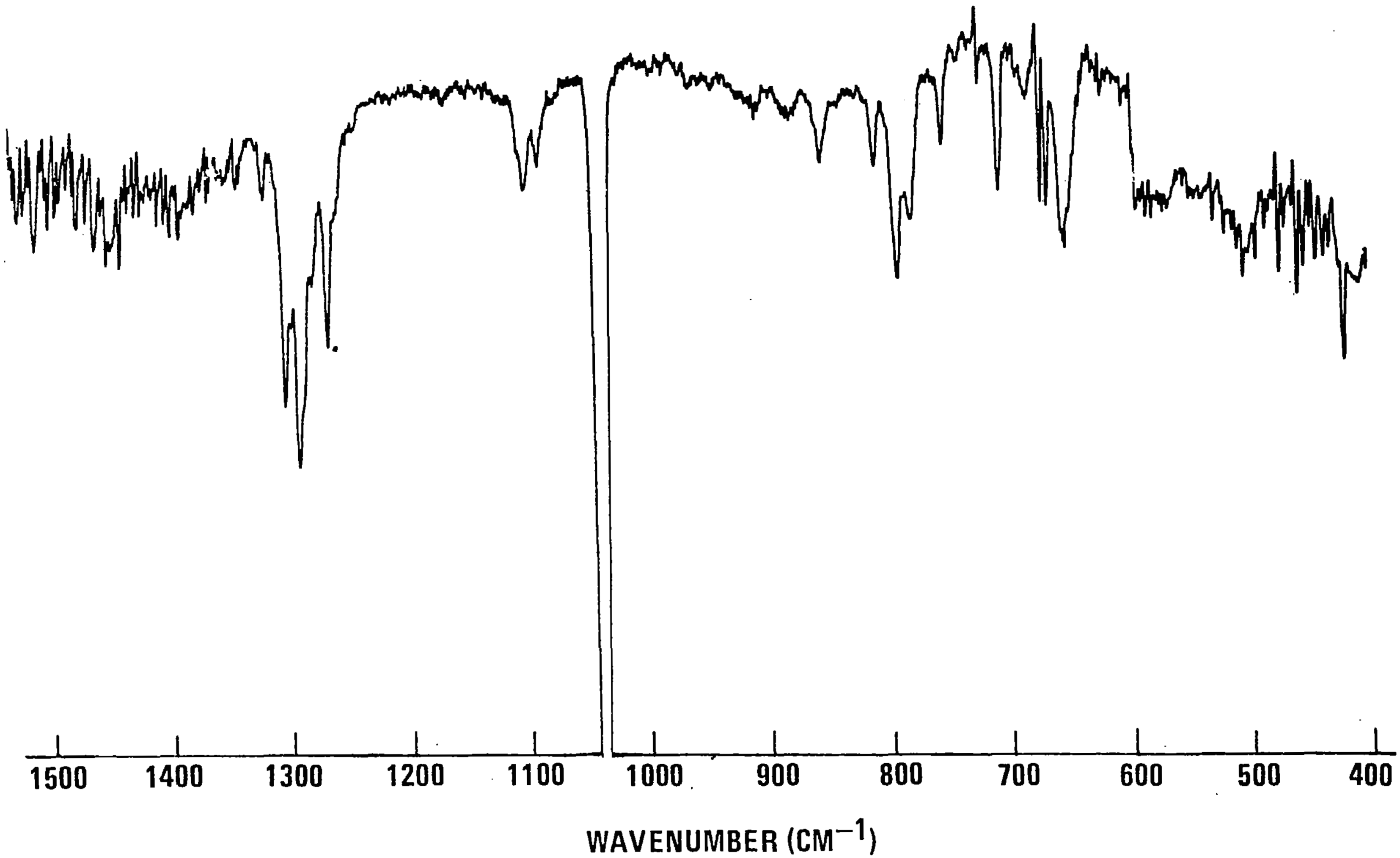


Figure 1. The IR spectrum of the reaction of Cl atoms and ozone.

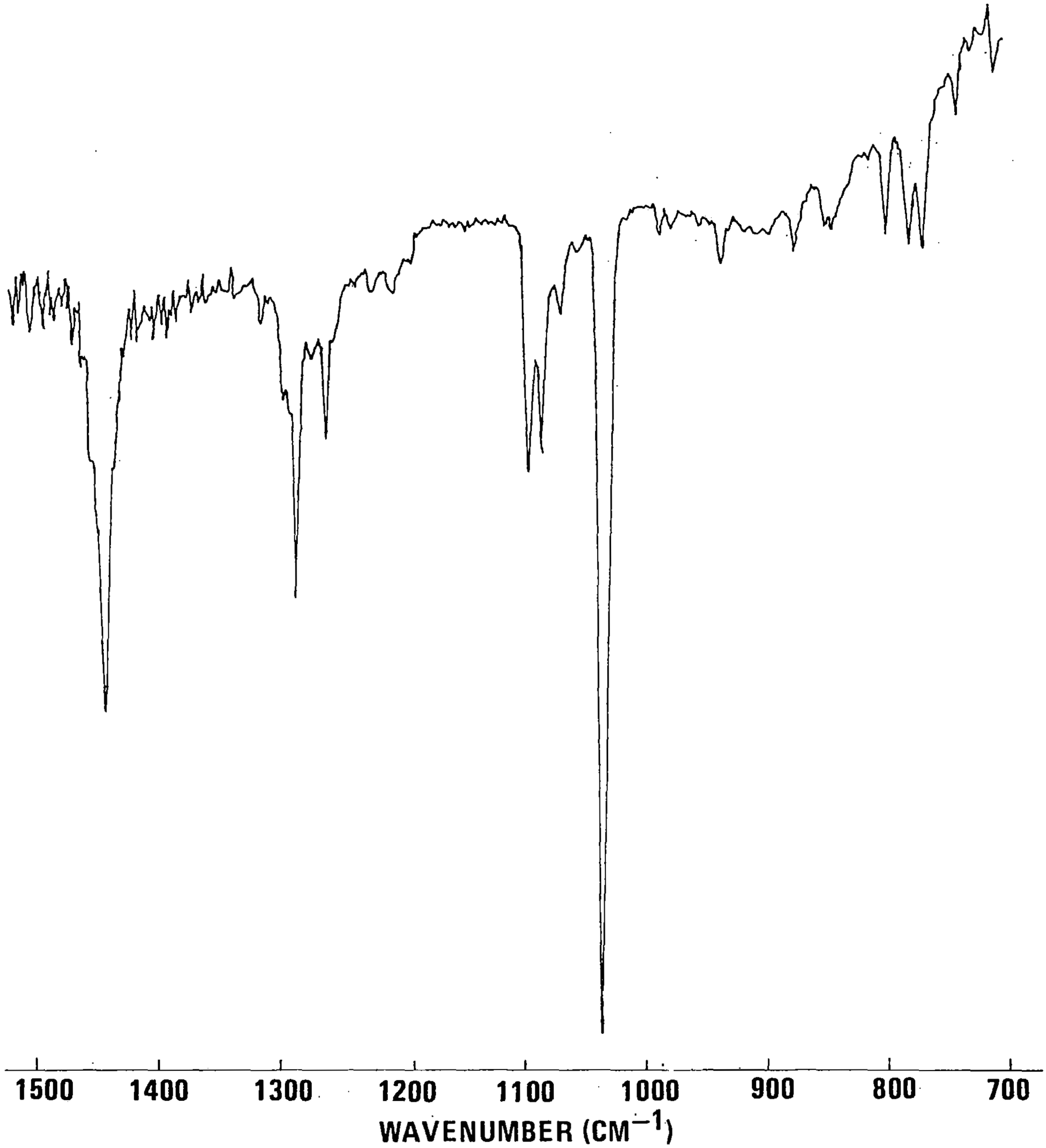


Figure 2. The IR spectrum of the reaction of Cl atoms and oxygen. The ozone absorptions observed at 1050 and 700 cm$^{-1}$ are due to the reaction of excited argon and oxygen. We observed production of $O_3$ when argon was discharged and then allowed to react with pure $O_2$ atoms. The mechanism appears to be $Ar^* + O_2 \rightarrow Ar + 2O$, and $2O + 2O_2 \rightarrow 2O_3$.

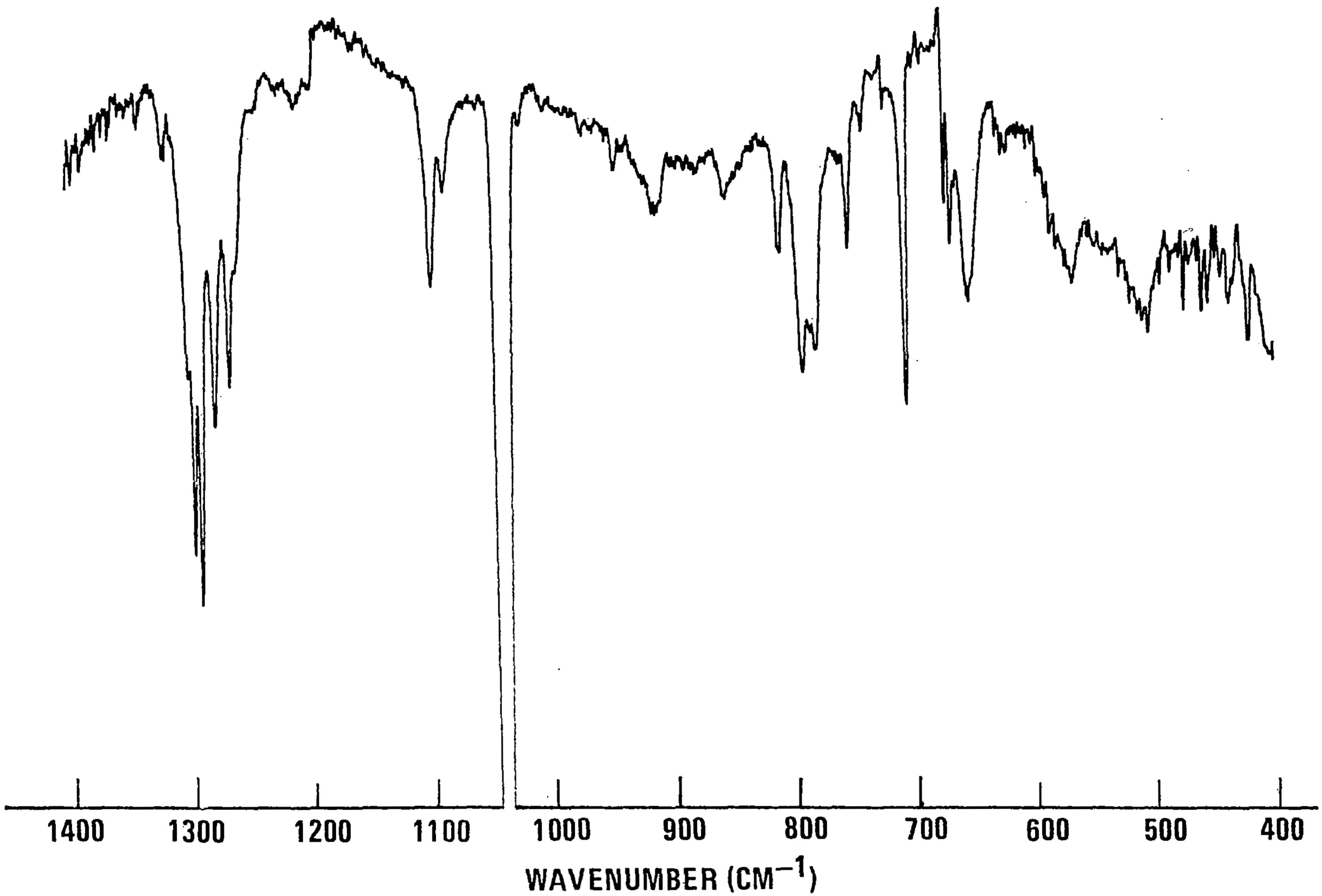


Figure 3. The IR spectrum of the reaction of Cl atoms and an $O_3/O_2$ mixture (1:10).

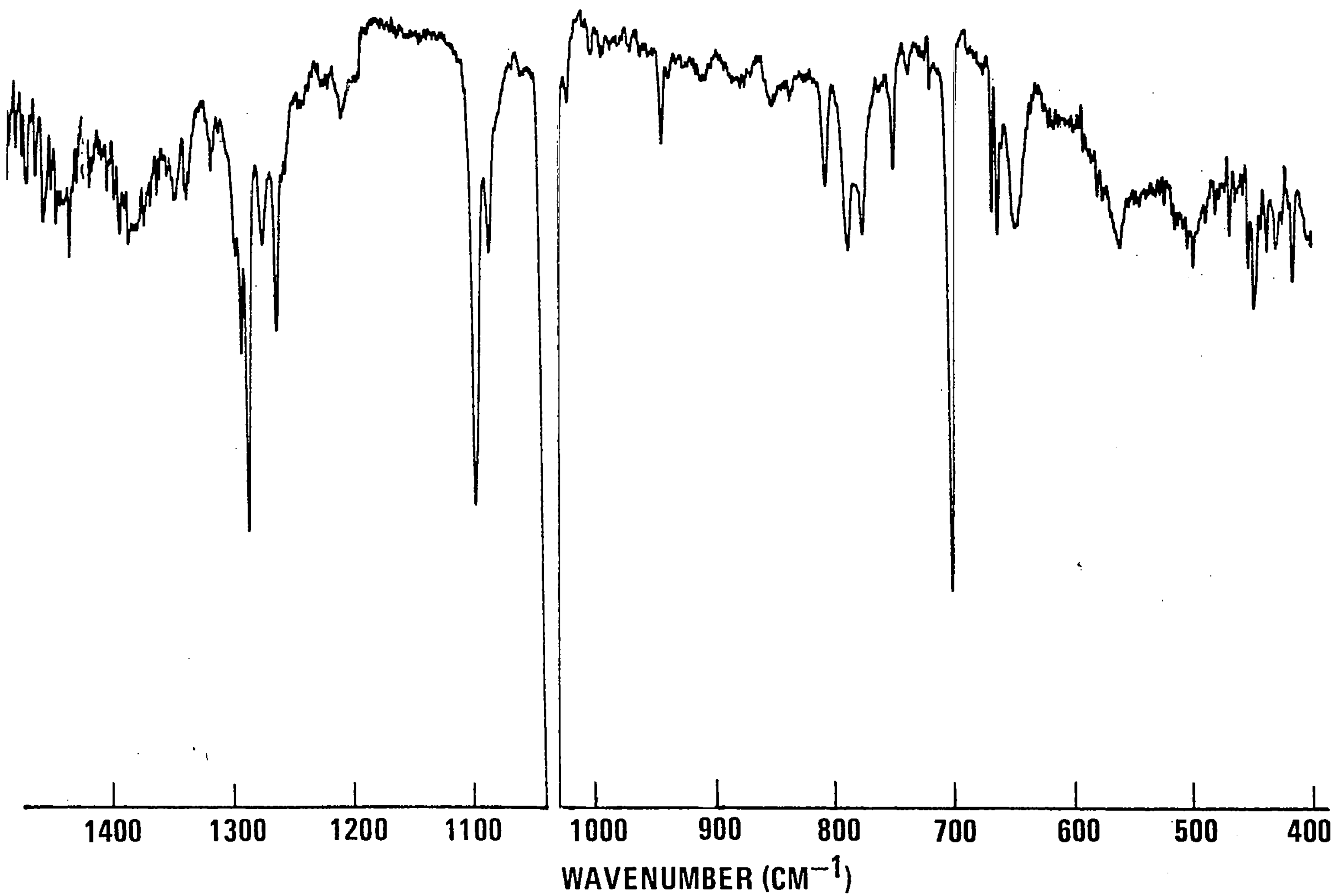


Figure 4. The IR spectrum of the reaction of Cl atoms and an $O_3/O_2$ mixture (1:20).

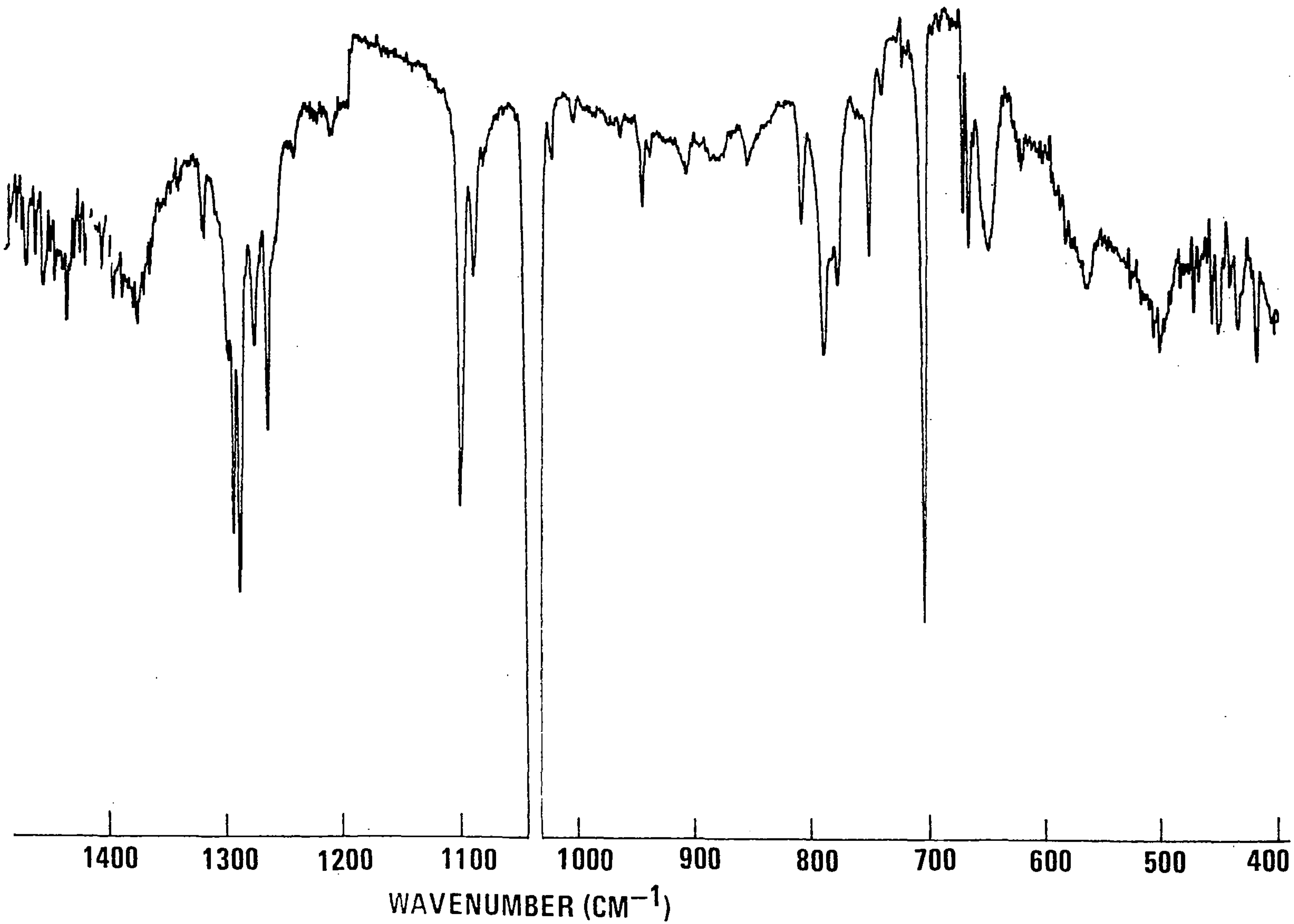


Figure 5. The IR spectrum of the reaction of Cl atoms and an $O_3/O_2$ mixture (1:60).

naturally, employed the same ozone concentrations, with successively increasing oxygen concentrations. Figure 3 represents the $O_3/O_2$ experiment of ratio 1:10. We see that the OClO (100 and 940 $cm^{-1}$) [5] production is greatly enhanced when compared to that from the reaction of Cl and pure $O_3$. The radical ClO (850 $cm^{-1}$) [6] is also present, together with $ClO_x$ species. Note that no ClOO (1442 $cm^{-1}$) [5] is produced. The OClO production increases in the $O_3/O_2$, 1:20 experiment (Fig. 4), and the OClO absorption for the 1:60 experiment (Fig. 5) is essentially the same for the 1:20 experiment.

That OClO is produced via a ClO intermediate, we propose

$$\begin{array}{l} Cl + O_3 \rightarrow ClO + O_2 \\ ClO + O_3 \rightarrow OClO + O_2 \\ \hline Cl + 2O_3 \rightarrow OClO + 2O_2 \text{ (net)} \end{array} \qquad (I)$$

and that chlorine atoms react with $O_2$ and a third body to produce ClOO

$$Cl + O_2 + M \rightarrow ClOO + M$$

However, the reaction mechanism involving the production enhancement of OClO when $O_2$ is present is not as evident. The mechanism may involve an asymmetrical $ClO_3$ (OOClO) intermediate, formed by the reaction of ClO and $O_2$

$$M + ClO + O_2 \rightarrow OOClO + M,$$

which can, in turn, react with $O_3$ to give OClO

$$OOClO + O_3 \rightarrow OClO + O_2$$

The net reaction is the same as for reaction scheme (I): $Cl + 2O_3 \rightarrow OClO + 2O_2$.

Interestingly, Zahniser, Kaufman, and Anderson (ZKA) [7] propose that asymmetrical $ClO_3$ and not symmetrical $ClO_3$ may be a product of the $Cl + O_3$ reaction. The proposed mechanism is

$$Cl + O_2 + M \rightleftarrows ClOO + M$$

$$ClOO + O_3 \rightarrow OClOO + O_2$$

Our results lead us to postulate asymmetrical $ClO_3$ in order to explain the oxygen enhancement of the OClO production. Also, if the ZKA scheme were correct, it is plausible to assume that unless the second reaction were extremely fast, relative to the first, we should see some ClOO at all times in our experiments, but we do not.

## IV. SUMMARY

The notable observations are: (1) the reaction of Cl atoms and $O_3$ produces primarily OClO, (2) the reaction of Cl atoms and $O_2$ produces primarily ClOO, (3) oxygen enhances the production of OClO in the $Cl + O_3$ reactions, and (4) the radical, ClO, is an intermediate in these gas phase reactions.

Attempts are now under way to identify and characterize the OOClO radical as well as the $ClO_x$ species which absorb in the regions 1300 $cm^{-1}$ to 1245 $cm^{-1}$ and 800 $cm^{-1}$ to 740 $cm^{-1}$.

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